Electronic Supplementary Information

for

Activation of O_2 Across a C(sp^3)-C(sp^3) Bond

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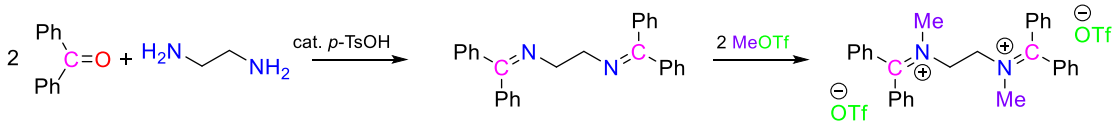
Experimental Details

General Considerations

All experiments were carried out under an N_2 atmosphere using standard Schlenk techniques or in a PL-HE-2GB Innovative Technology GloveBox, unless otherwise stated. *n*-Hexane, diethyl ether, THF, and toluene were dried by PS-MD-5 Innovative Technology solvent purification system or common drying solvent technique. All other chemicals were purchased commercially (ethylenediamine – AVRA Laboratories, benzophenone – AVRA Laboratories, benzaldehyde – AVRA Laboratories potassium - Sigma Aldrich, graphite -Sigma Aldrich, *p*-toluenesulfonic acid– Sigma Aldrich, methyl triflate – Sigma Aldrich, silver triflate – Sigma Aldrich, and nitrosonium hexafluoroantimonate – Sigma Aldrich) and used as received. KC_8 was prepared according to the literature procedure.[S1] Benzene-d_6 was dried and distilled over potassium under argon. Acetonitrile-d_3, chloroform-d_1, and dichloromethane-d_2 were dried and distilled over CaH_2 under argon. NMR spectra were recorded on a BrukerNanoBay 300 MHz NMR spectrometer. ^1H and $^{13}C\{^1H\}$ NMR spectra were referenced to the peaks of residual protons of the deuterated solvent (^1H) or the deuterated solvent itself ($^{13}C\{^1H\}$). $^{19}F\{^1H\}$ NMR spectra were referenced to external tol-CF_3. The FT-IR spectrum was recorded on a Bruker–Alpha spectrometer. Elemental analyses (C, H, N, and S) were carried out with an Elementar Vario MICRO elemental analyzer. Melting points were determined in closed NMR tubes under argon atmosphere and are uncorrected.

Synthesis of 3

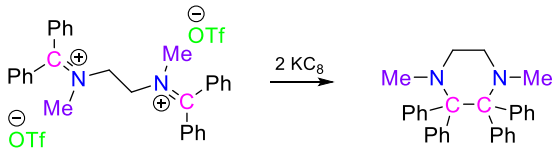


3

a) Benzophenone (10 g, 54.8 mmol) in toluene (100.0 mL) and catalytic amounts of *p*-toluenesulfonic acid monohydrate (200.0 mg, 1.05 mmol) were added to a 250 mL Schlenk flask and stirred for half an hour at room temperature. Then ethylenediamine (1.8 mL, 26.1 mmol) was added dropwise to it. The resulting mixture was refluxed using a Dean-Stark apparatus for 2 hours at 100 °C and 10 hours at 170 °C. After completion of the reaction, the solvents were removed under reduced pressure. The resulting light-yellow colored solid was dissolved in CH_2Cl_2 and washed with saturated $NaHCO_3$ solution (3×50 mL). The organic portions were dried over anhydrous Na_2SO_4 and evaporated to give a white crystalline solid. This crude product *N,N'*-

bis(diphenylmethylene)-ethylenediamine was purified by crystallization in CH_2Cl_2 to obtain white spongy crystals. **Yield:** 5.68 g (14.6 mmol, 56 %). **M.P.:** 118 °C (melted). **^{1}H** NMR ($CDCl_3$, 25 °C, 300 MHz): δ = 7.59−7.56 (d, 4H, *J* = 7.6 Hz, *o*-Ar-*H*), 7.44−7.42 (m, 6H, *m* & *p*-Ar-*H*), 7.36−7.28 (m, 6H, *m* & *p*-Ar-*H*), 7.15−7.13 (d, 4H, *J* = 7.6 Hz, o-Ar-*H*), 3.76 (s, 4H, CH_2-CH_2) ppm. **^{13}C{^{1}H}** NMR ($CDCl_3$, 25 °C, 75 MHz): δ = 168.86 (*C*=N), 140.00 (*ipso*-Ar-*C*), 137.02 (*ipso*-Ar-*C*), 129.94 (Ar-*C*), 128.54 (Ar-*C*), 128.50 (Ar-*C*), 128.40 (Ar-*C*), 128.10 (Ar-*C*), 128.07 (Ar-*C*), 55.25 (*C*H_2-*C*H_2) ppm. b) A solution of MeOTf (2.1 g, 1.4 mL, 12.87 mmol, in 20 mL of DCM) in a 50 mL Schlenk flask was added slowly to the solution of *N,N'*-bis(diphenylmethylene)-ethylenediamine (2.0 g, 5.14 mmol, in 50 mL DCM) in a 100 mL Schlenk flask at −78 °C. After the completion of addition, the reaction mixture slowly warmed up to room temperature and was stirred at room temperature overnight. Evaporation of the solvent resulted in a white residue. The residue was washed with 50 mL of Et_2O to obtain pure **3** as white powder. After crystallization of **3** from acetonitrile with Et_2O diffusion at room temperature, we obtained single crystals suitable for an X-ray diffraction study after one day. **Yield:** 2.58 g (3.6 mmol, 70 %). **M.P.:** 189 °C (melted). **^{1}H NMR** (CD_3CN, 25 °C, 300 MHz): δ = 7.75−7.70 (t, 4H, *J* = 8.2 Hz, *p*-Ar-*H*), 7.60−7.53 (m, 8H, *m*-Ar-*H*), 7.47−7.45 (d, 4H, *J* = 7.8 Hz, *o*-Ar-*H*), 7.37-7.35 (d, 4H, *J* = 7.8 Hz, *o*-Ar-*H*), 4.56 (s, 4H, CH_2-CH_2), 3.68 (s, 6H, NCH_3) ppm. **^{13}C{^{1}H} NMR** (CD_3CN, 25 °C, 75 MHz): δ = 188.62 (*C*=N), 135.52 (Ar-*C*), 134.85 (Ar-*C*), 133.97 (Ar-*C*), 133.90 (Ar-*C*), 131.68 (Ar-*C*), 130.53 (Ar-*C*), 130.08 (Ar-*C*), 130.02 (Ar-*C*), 55.99 (*C*H_2-*C*H_2), 46.95 (NCH_3) ppm. **^{19}F{^{1}H} NMR** (CD_3CN, 25 °C, 282 MHz): δ = −79.24 ppm. **Elemental analysis** calcd. (%) for $C_{32}H_{30}N_2F_6O_6S_2$: C, 53.63; H, 4.22; N, 3.91; S, 8.95. found: C, 53.74; H, 4.17; N, 4.07; S, 9.20.

Synthesis of 1

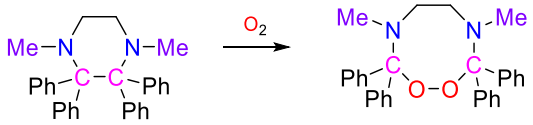


3 **1**

About 50 mL of THF was added to a 100 mL Schlenk flask containing **3** (2 g, 2.79 mmol) and KC_8 (1.13 g, 8.37 mmol) at −78 °C. After stirring at −78 °C for 1 hour, the reaction mixture was slowly brought to room temperature and stirred at room temperature overnight. After completion of the reaction, all volatiles were removed under vacuum and the resulting residue was extracted using hexane. After removing the solvent product **1** was obtained as colorless crystalline solid. A saturated hexane solution of **1** was kept at room temperature resulting in single crystals suitable

for an X-ray diffraction study after one day. **Yield:** 0.899 g (1.81 mmol, 77 %). **M.P.:** 146 °C (melted). **^{1}H NMR** (C_6D_6, 25 °C, 300 MHz): *δ* = 8.26 (br-s, 3H, Ar-*H*), 7.16-7.06 (br-s, 6H, Ar-*H*), 7.06–7.04 (m, 4H, Ar-*H*), 6.97–6.92 (t, 3H, *J* = 6.8 Hz, Ar-*H*), 6.79 (br-s, 2H, Ar-*H*), 6.50 (br-s, 2H, Ar-*H*), 2.70 (d, 2H, *J* = 7.8 Hz, axial C*H*$_2$-C*H*$_2$), 2.45 (d, 2H, *J* = 7.8 Hz, equatorial C*H*$_2$-C*H*$_2$), 1.72 (s, 6H, NC*H*$_3$) ppm. **^{13}C{^{1}H} NMR** (C_6D_6, 25 °C, 75 MHz): *δ* = 137.84 (*axial-ipso*-Ar-*C*), 134.15 (*equatorial-ipso*-Ar-*C*), 127.22 (Ar-*C*H), 126.33 (Ar-*C*H), 125.32 (Ar-*C*H), 79.16 (*ipso*-Ar$_2$*C*N), 49.27 (*C*H$_2$-CH$_2$), 41.67 (N*C*H$_3$) ppm. **^{1}H NMR** ($CDCl_3$, 25 °C, 300 MHz): δ = 8.10 (br-s, 3H, Ar-H), 7.59-7.13 (m, 12H, Ar-H), 6.85 (br-s, 3H, Ar-H), 6.23 (br-s, 2H, Ar-H), 2.75-2.66 (2×t-merged, 4H, CH$_2$-CH$_2$), 1.76 (s, 6H, NCH$_3$) ppm. **^{1}H NMR** (CD_2Cl_2, 25 °C, 300 MHz): δ = 8.11 (br-s, 4H, Ar-H), 7.17-7.11 (m, 12H, Ar-H), 6.85 (br-s, 2H, Ar-H), 6.23 (br-s, 2H, Ar-H), 2.77-2.71 (t, 2H, CH$_2$-CH$_2$), 2.70-2.65 (t, 2H, CH$_2$-CH$_2$) 1.73 (s, 6H, NCH$_3$) ppm. **Elemental analysis** calcd. (%) for $C_{30}H_{30}N_2$: C, 86.08; H, 7.22; N, 6.69. found: C, 85.20; H, 6.79; N, 6.75.

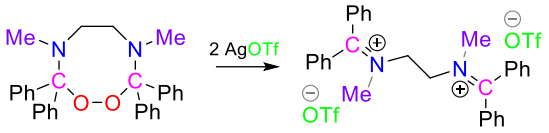
Synthesis of 2



1 **2**

To a 50 mL Schlenk flask containing **1** (225 mg, 0.537 mmol), 20 mL of hexane was added and the solution was refluxed under an open atmosphere. A saturated hexane solution of **2** was kept at room temperature resulting in single crystals suitable for an X-ray diffraction study after 2 days. **Yield:** 200 mg (0.443 mmol, 82 %). **M.P.:** 153 °C (decomposed). **^{1}H NMR** (C_6D_6, 25 °C, 300 MHz): *δ* = 8.03 (br.s, 3H, Ar-*H*), 7.73–7.71 (d, 4H, Ar-*H*), 7.26–7.21 (t, 4H, *J* = 7.6 Hz, Ar-*H*), 7.09-7.02 (m, 6H, Ar-*H*), 7.00-6.92 (m, 3H, Ar-*H*), 3.64-3.60 (d, 2H, *J* = 12.0 Hz axial C*H*$_2$-C*H*$_2$), 2.47 (s, 6H, NC*H*$_3$), 2.36-2.40 (d, 2H, *J* = 12.0 Hz, equatorial C*H*$_2$-C*H*$_2$), ppm. **^{13}C{^{1}H} NMR** (C_6D_6, 25 °C, 75 MHz): *δ* = 145.21 (*axial-ipso*-Ar-*C*), 144.18 (equatorial-*ipso*-Ar-*C*), 128.55 (Ar-*C*H), 128.53 (Ar-*C*H), 127.31 (Ar-*C*H), 127.09 (Ar-*C*H), 126.92 (Ar-*C*H), 103.34 (*ipso*Ar$_2$*C*NO), 46.79 (*C*H$_2$-*C*H$_2$), 37.63 (N*C*H$_3$) ppm. **FT-IR** (KBr, cm^{-1}): ῡ = 3448(br), 1635(s), 877(w), 830(w), 746(m), 704(s), 636(w), 547(w). **Elemental analysis** calcd. (%) for $C_{30}H_{30}N_2O_2$: C, 79.97; H, 6.71; N, 6.22. found: C, 80.27; H, 6.73; N, 6.37.

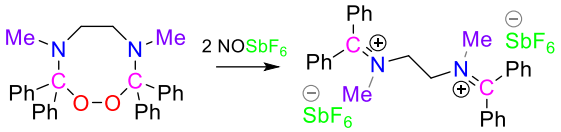
1:2 Reaction of 2 and AgOTf



2 **3**

About 15 mL of CH_2Cl_2 was added under N_2 atmosphere to a 25 mL Schlenk flask containing **2** (100 mg, 0.222 mmol) and silver triflate (119 mg, 0.466 mmol) at room temperature and under stirring. After 2 hours of stirring, all volatiles were removed under vacuum and the resulting residue was extracted using acetonitrile. After removing the solvent, product **3** was obtained as colorless crystalline solid. **Yield:** 148 mg (93%).

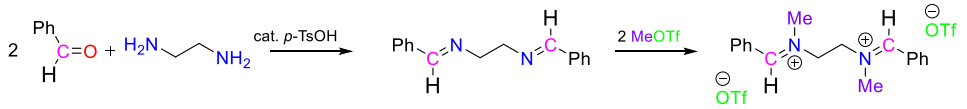
1:2 Reaction of 2 and $NOSbF_6$



2 **$3^{(SbF_6)_2}$**

About 15 mL of CH_2Cl_2 was added under N_2 atmosphere to a 25 mL Schlenk flask containing **2** (100 mg, 0.222 mmol) and nitrosonium hexafluoroantimonate (123 mg, 0.466 mmol) at room temperature and under stirring. After 5 minutes the colorless solution turned yellow. After 30 minutes of stirring, all the volatiles were removed under vacuum and the resulting residue was extracted using acetonitrile. After removing the solvent product $\mathbf{3}^{(SbF_6)_2}$ was obtained as light orange crystalline solid. **Yield**: 187 mg (95%). **M.P.:** >200°C. **^{1}H NMR** (CD_3CN, 25 °C, 300 MHz): δ = 7.79−7.74 (t, 4H, J = 8.2 Hz, p-Ar-*H*), 7.64−7.57(m, 8H, m -Ar-*H*), 7.46−7.44 (d, 4H, J = 7.8 Hz, o-Ar-*H*), 7.35-7.33 (d, 4H, J = 7.8 Hz, o-Ar-*H*), 4.51 (s, 4H, CH_2-CH_2), 3.68 (s, 6H, NCH_3) ppm. **^{13}C{^{1}H} NMR** (CD_3CN, 25 °C, 75 MHz): δ = 188.74 (*C*=N), 135.68 (Ar-*C*), 134.97 (Ar-*C*), 133.80 (Ar-*C*), 133.69 (Ar-*C*), 131.73 (Ar-*C*), 130.50 (Ar-*C*), 130.11 (Ar-*C*), 130.01 (Ar-*C*), 55.82 (*C*H2-*C*H2), 46.82(NCH_3) ppm. **^{19}F{^{1}H} NMR** (CD_3CN, 25 °C, 282 MHz): δ = −123.77 (sextet, ^1J(^{121}Sb, ^{19}F) = 1944 Hz), −123.85 (octet, ^1J(^{123}Sb, ^{19}F) = 1028 Hz) ppm.

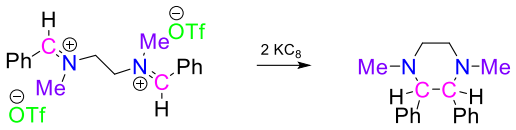
Synthesis of 4



4

a) Anhydrous sodium sulfate (56.8 g, 400 mmol) was placed in a 500 mL round bottle flask and diethyl ether (250 mL) was added. Benzaldehyde (16.0 mL, 157.23 mmol) and a catalytic amount of p-toluenesulfonic acid were added to the flask at room temperature and then stirred for 10 minutes. Then ethylenediamine (5.0 mL, 74.87 mmol) was added dropwise to the solution with stirring at 0 °C temperature followed by 12 hours at room temperature. After completion of the reaction, the reaction mixture was filtered through a funnel containing anhydrous sodium sulfate over cotton. Sodium sulfate was washed with diethyl ether (3x20 mL) and filtered. The combined ether layers were collected. Solvent and other volatiles were removed under reduced pressure to obtained a light yellow colored solid as desired product. This crude product *N,N'*-(ethane-1,2-diyl)-bis(1-phenylmethanimine) was purified by crystallization in hexane to obtain colorless crystals. **Yield:** 15.03 g (63.64 mmol, 85%). **M.P.:** 42 °C (melted). **^{1}H NMR** ($CDCl_3$, 25 °C, 300 MHz): δ = 8.29 (s, 2H, C*H*=N), 7.71−7.68 (d, 4H, *J* = 7.6 Hz, o-Ar-*H*), 7.39−7.38 (m, 6H, m, p-Ar-*H*), 3.98 (s, 4H, CH_2-CH_2) ppm. **^{13}C{^{1}H} NMR** ($CDCl_3$, 25 °C, 75 MHz): δ = 162.81 (*C*=N), 136.23 (*ipso*-Ar-*C*), 130.72 (Ar-*C*), 128.65 (Ar-*C*), 128.19 (Ar-*C*), 61.73 (*C*H2-*C*H2) ppm. b) A solution of MeOTf (5.20 g, 3.5 mL, 31.73 mmol, in 15 mL of DCM) in a 25 mL Schlenk flask was added slowly to the solution of *N,N'*-(ethane-1,2-diyl)-bis(1-phenylmethanimine) (3.0 g, 12.69 mmol, in 50 mL DCM) in a 100 mL Schlenk flask at −78 °C. After the completion of addition, the reaction mixture slowly warmed up to room temperature and was stirred overnight. With the evaporation of the solvent a white residue formed. The residue was washed with 50 mL of Et_2O to obtain pure **4** as white powder. After diffusion of diethyl ether to a saturated acetonitrile solution of **4** at room temperature, suitable single crystals for a X-ray diffraction study were obtained after one day. **Yield:** 4.65 g (8.25 mmol, 65%). **M.P.:** 180°C. **^{1}H NMR** (CD_3CN, 25 °C, 300 MHz): δ = 9.22 (s, 2H, C*H*=N), 8.05−8.02 (d, 4H, *J* = 7.8 Hz, p-Ar-*H*), 7.94−7.89 (t, 2H, *J* = 7.6 Hz, p -Ar-*H*), 7.79−7.74 (t, 4H, *J* = 7.6 Hz, m-Ar-*H*), 4.65 (s, 4H, CH_2-CH_2), 3.93 (s, 6H, NCH_3) ppm. **^{13}C{^{1}H} NMR** (CD_3CN, 25 °C, 75 MHz): δ = 176.41 (*C*=N), 138.18 (*ipso*-Ar-*C*), 134.91 (Ar-*C*), 130.82 (Ar-*C*), 128.00 (Ar-*C*), 61.20 (*C*H2-*C*H2), 43.90 (NCH_3) ppm. **^{19}F{^{1}H} NMR** (CD_3CN, 25 °C, 282 MHz): δ = −79.24 ppm. **Elemental analysis** calcd. (%) for $C_{20}H_{22}N_2F_6O_6S_2$: C, 42.55; H, 3.93; N, 4.96; S, 11.36. found: C, 41.44; H, 3.70; N, 5.27; S, 11.61.

Synthesis of 5



4 **5**

About 50 mL of THF was added to a 100 mL Schlenk flask containing **4** (1 g, 1.77 mmol) and KC_8 (0.598 g, 4.42 mmol) at −78 °C. After stirring at −78 °C for 1 hour, the reaction mixture was slowly brought to room temperature and stirred overnight. After completion of the reaction, all volatiles were removed under vacuum and the resulting residue was extracted using hexane. After removing the solvent product **5** was obtained as colorless crystalline solid. A saturated hexane solution of **5** was kept at room temperature to yield single crystals suitable for an X-ray diffraction study. **Yield:** 330 mg (1.24 mmol, 70%). **M.P.:** 82°C (melted). **^{1}H NMR** (C_6D_6, 25 °C, 300 MHz): δ = 6.96 (br, 10H, Ar-*H*), 3.02 (s, 2H, C*H*-N), 2.79-2.77 (d, 2H, *J* = 7.4 Hz, axial CH_2-CH_2), 2.57-2.55 (d, 2H, *J* = 7.4 Hz, equatorial CH_2-CH_2), 1.98 (s, 6H, NCH_3) ppm. **^{13}C{^{1}H} NMR** (C_6D_6, 25 °C, 75 MHz): δ = 141.55 (^{ipso}Ar-*C*), 128.34 (Ar-*C*), 128.01 (Ar-*C*), 127.18 (Ar-*C*), 76.57 (*C*HN), 55.93 (*C*H2-*C*H2), 44.39 (N*C*H$_3$) ppm. **^{1}H NMR** ($CDCl_3$, 25 °C, 300 MHz): δ = 7.06 (br, 10H, Ar-*H*), 3.04-3.02 (d, 2H, *J* = 7.8 Hz, axial-CH_2-CH_2), 2.96 (s, 2H, C*H*-N), 2.63-2.60 (d, 2H, *J* = 7.8 Hz, equatorial CH_2-CH_2), 2.02 (s, 6H, NCH_3) ppm. **^{1}H NMR** (CD_2Cl_2, 25 °C, 300 MHz): δ = 7.07 (br, 10H, Ar-*H*), 2.98-2.96 (d, 2H, *J* = 7.8 Hz, axial-CH_2-CH_2), 2.94 (s, 2H, C*H*-N), 2.57-2.55 (d, 2H, *J* = 7.8 Hz, equatorial CH_2-CH_2), 1.95 (s, 6H, NCH_3) ppm. **Elemental analysis** calcd. (%) for $C_{18}H_{22}N_2$: C, 81.16; H, 8.32; N, 10.52. found: C, 81.12; H, 8.56; N, 10.29.

NMR Spectra

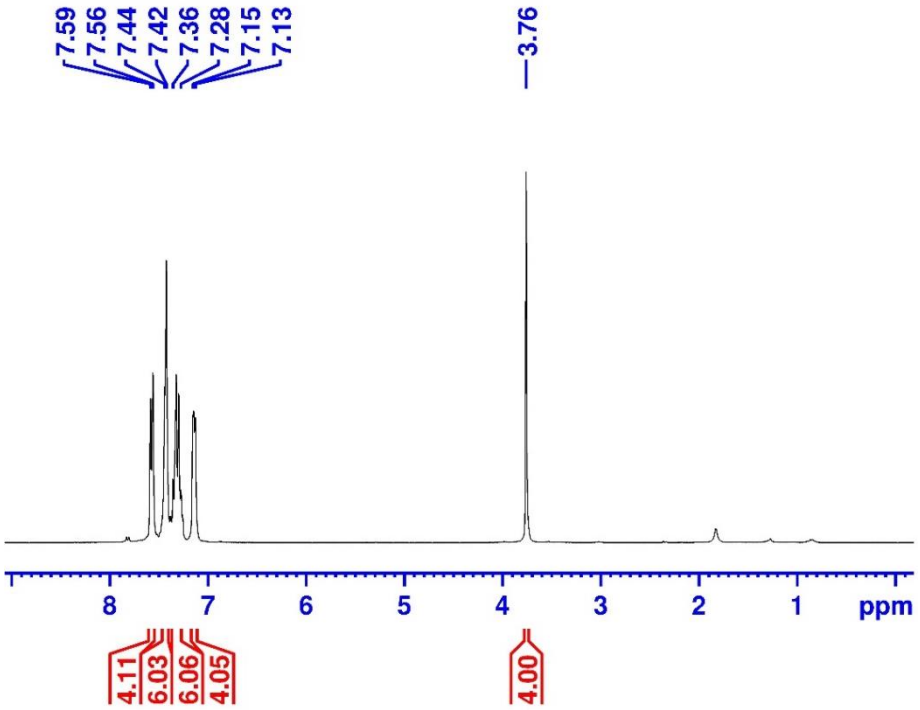


Fig. S1 ^{1}H NMR spectrum of compound *N,N'*-bis(diphenylmethylene)-ethylenediamine in $CDCl_3$ at room temperature.

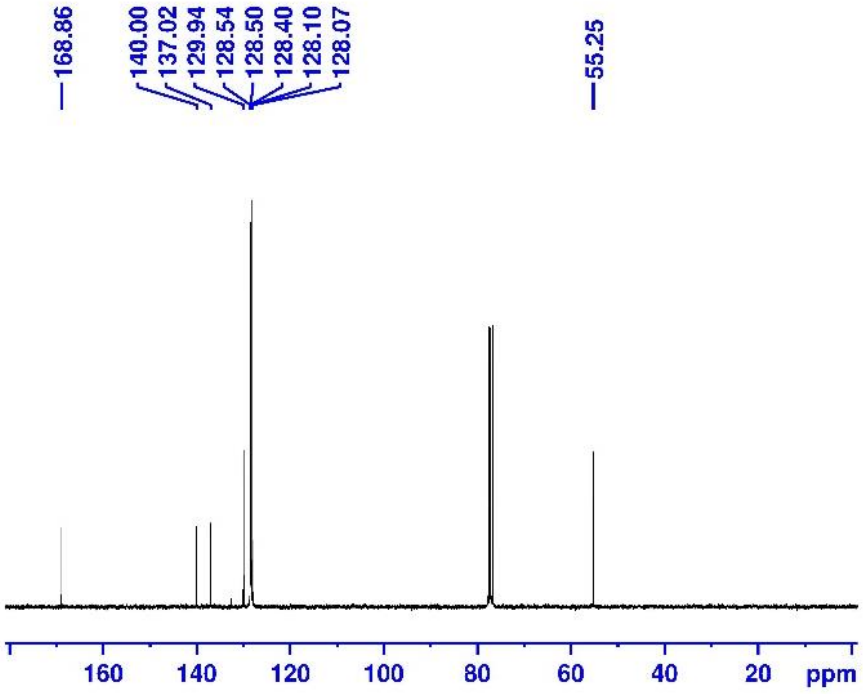


Fig. S2 $^{13}C\{^{1}H\}$ NMR spectrum of compound *N,N'*-bis(diphenylmethylene)-ethylenediamine in $CDCl_3$ at room temperature.

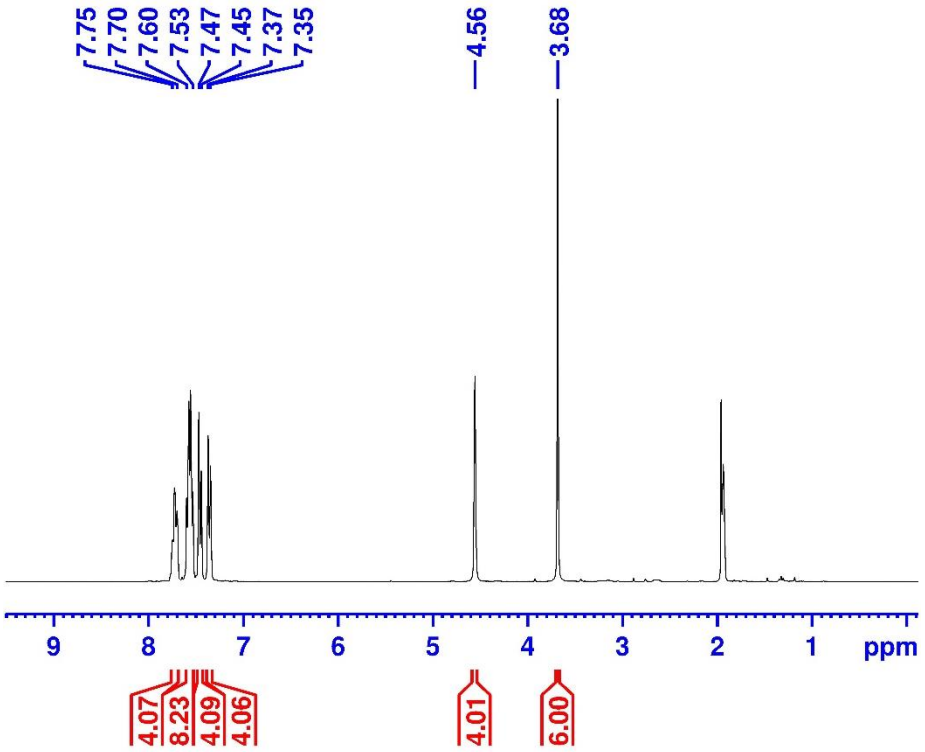


Fig. S3 ^{1}H NMR spectrum of compound **3** in CD_3CN at room temperature.

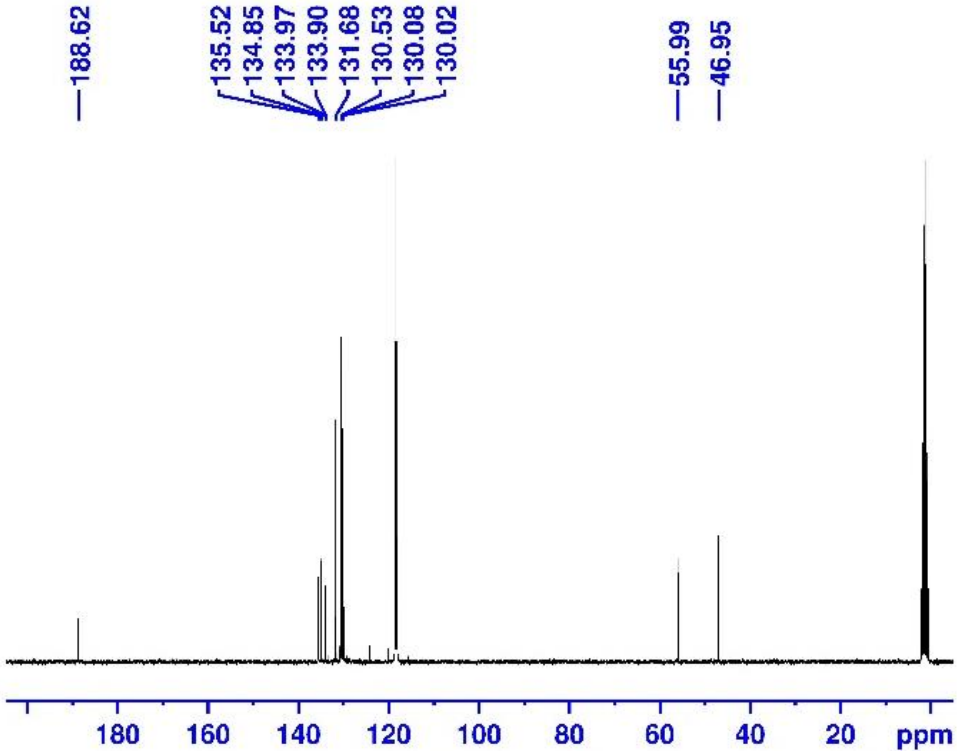


Fig. S4 $^{13}C\{^{1}H\}$ NMR spectrum of compound **3** in CD_3CN at room temperature.

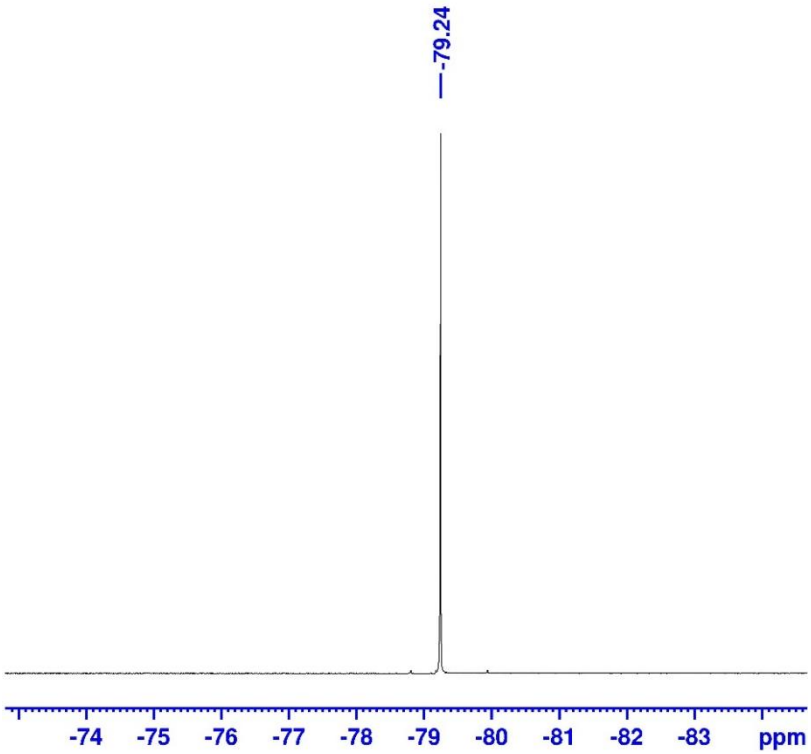


Fig. S5 $^{19}F\{1H\}$ NMR spectrum of compound **3** in CD_3CN at room temperature.

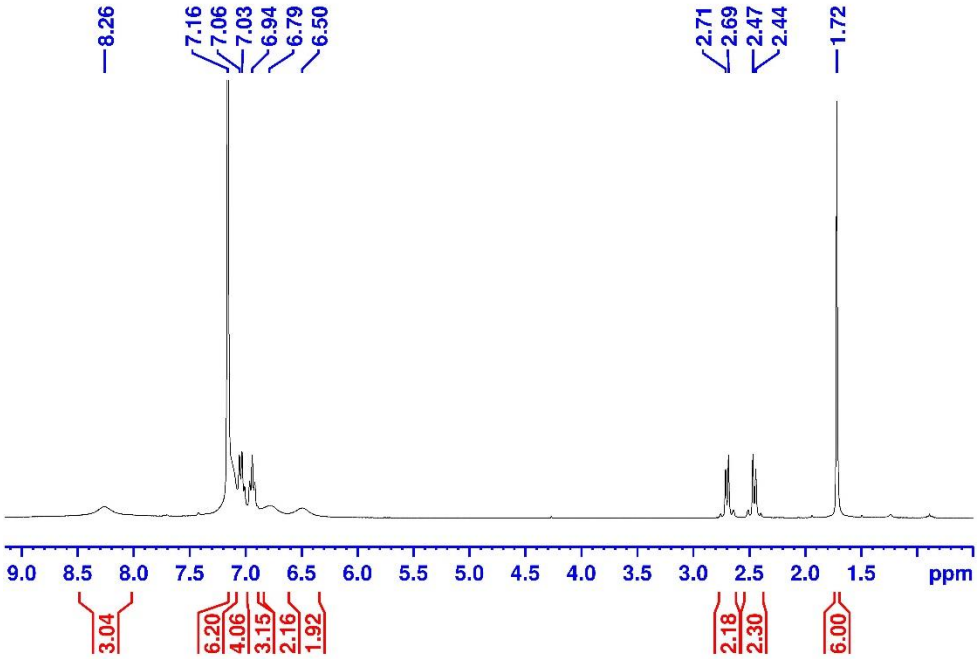


Fig. S6 ^{1}H NMR spectrum of compound **1** in C_6D_6 at room temperature.

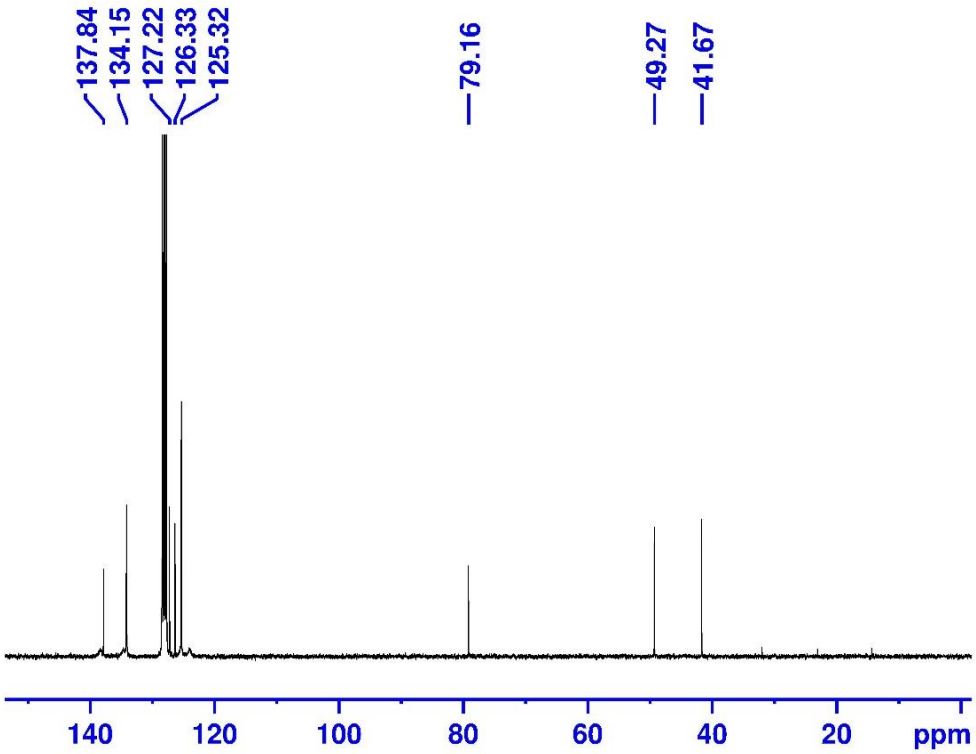


Fig. S7 $^{13}C\{^{1}H\}$ NMR spectrum of compound **1** in C_6D_6 at room temperature.

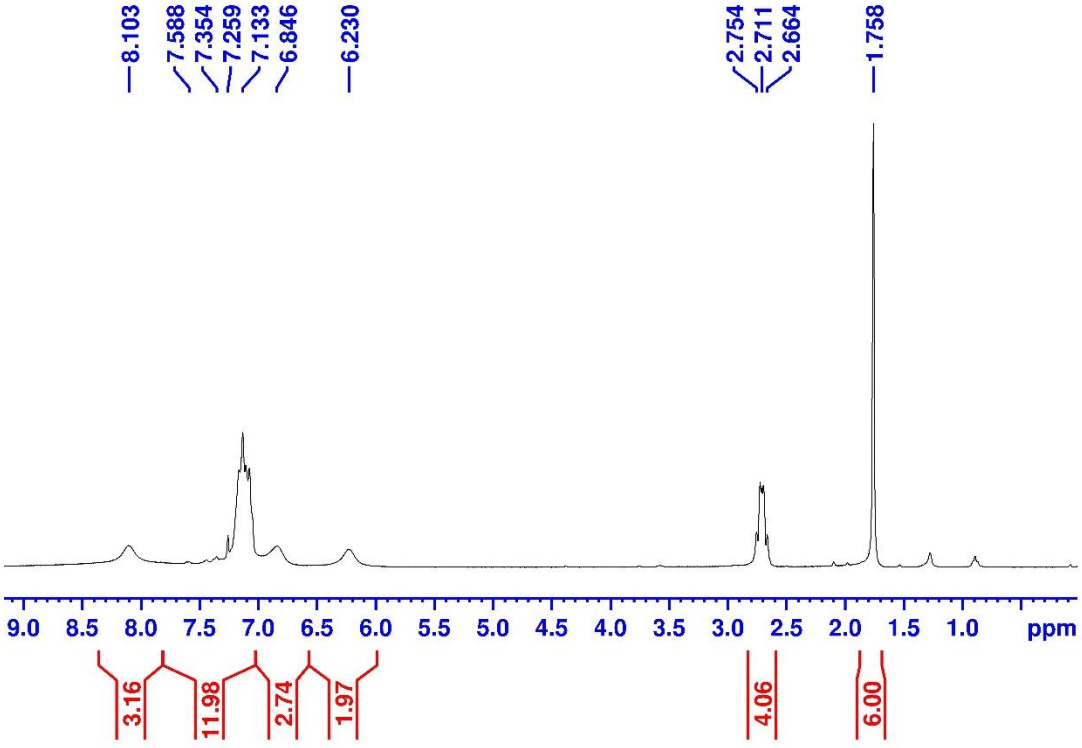


Fig. S8 ^{1}H NMR spectrum of compound **1** in $CDCl_3$ at room temperature.

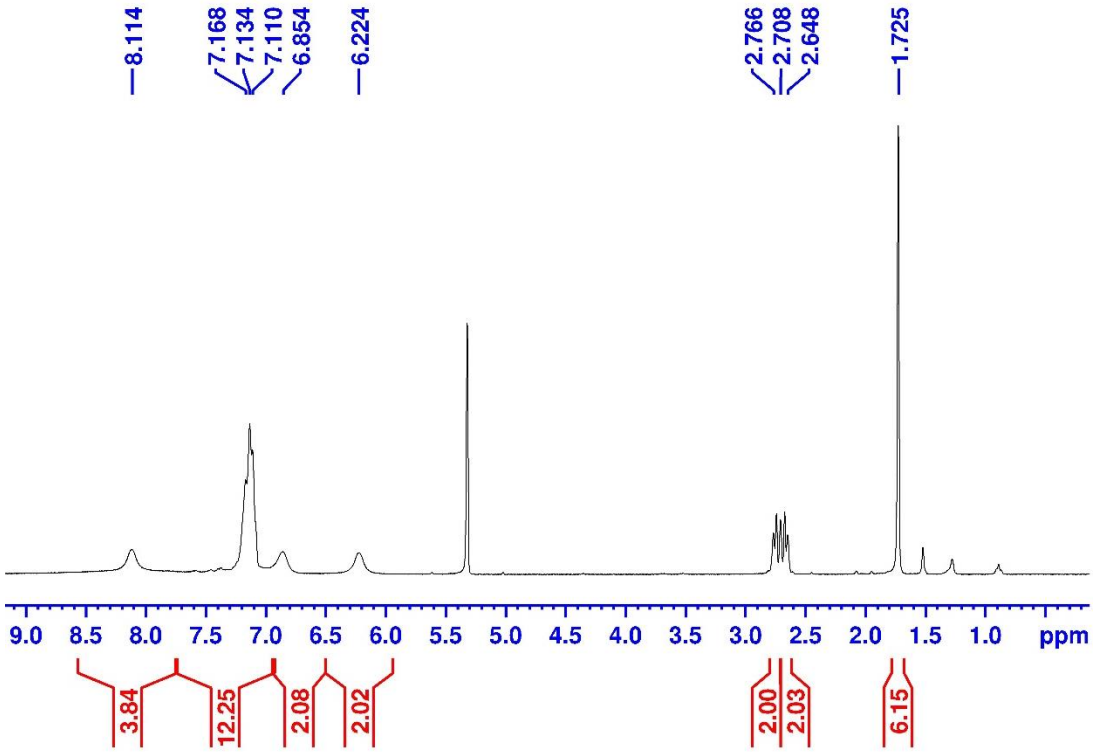


Fig. S9 ^{1}H NMR spectrum of compound **1** in CD_2Cl_2 at room temperature.

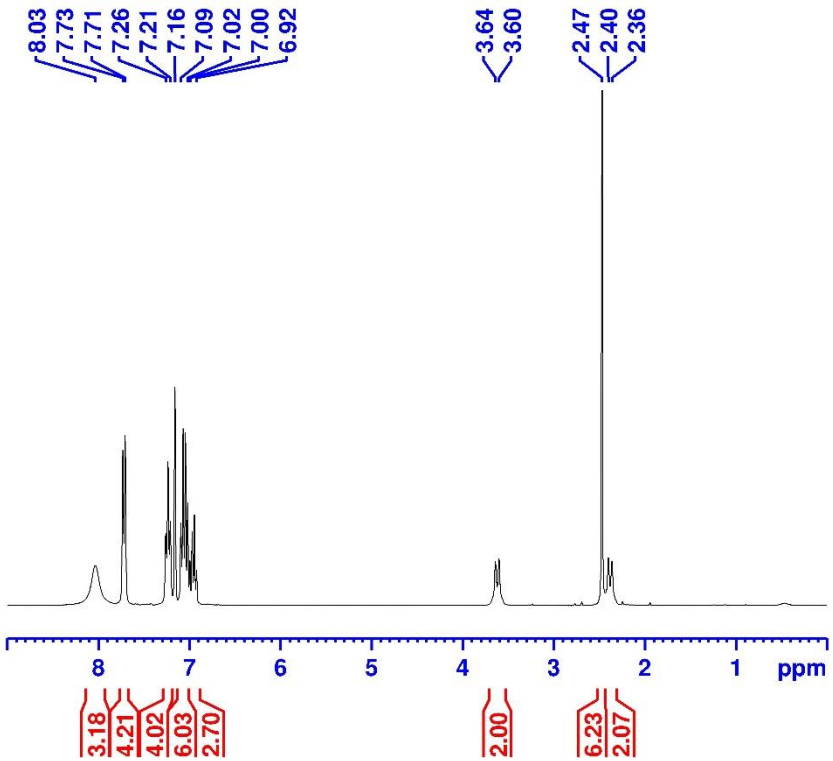


Fig. S10 ^{1}H NMR spectrum of compound **2** in C_6D_6 at room temperature.

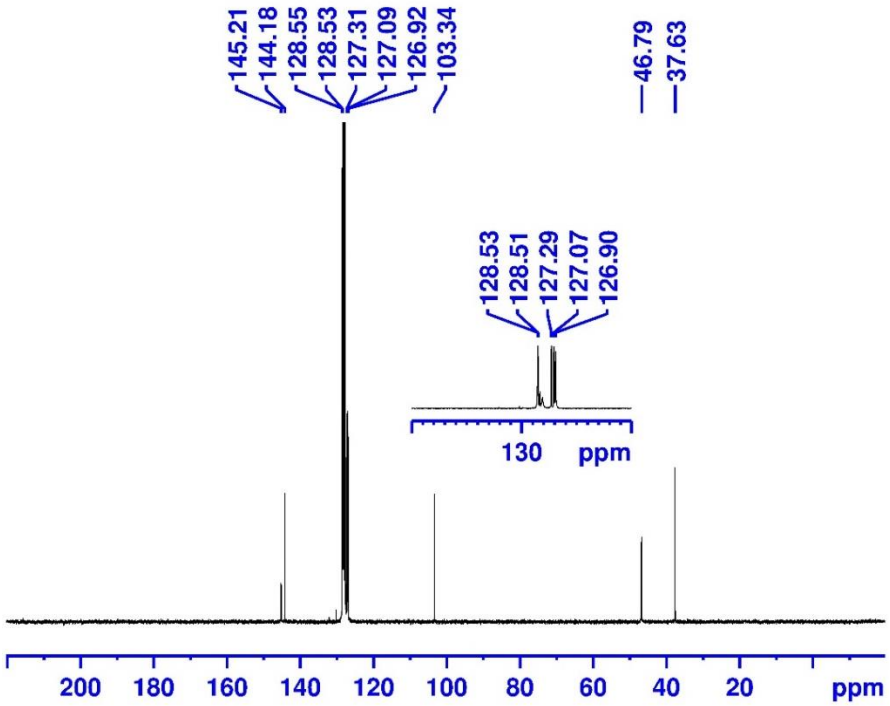


Fig. S11 $^{13}C\{^{1}H\}$ NMR spectrum of compound **2** in C_6D_6 at room temperature (Insert: Dept-90 to showcase the only aromatic C-*H* resonances).

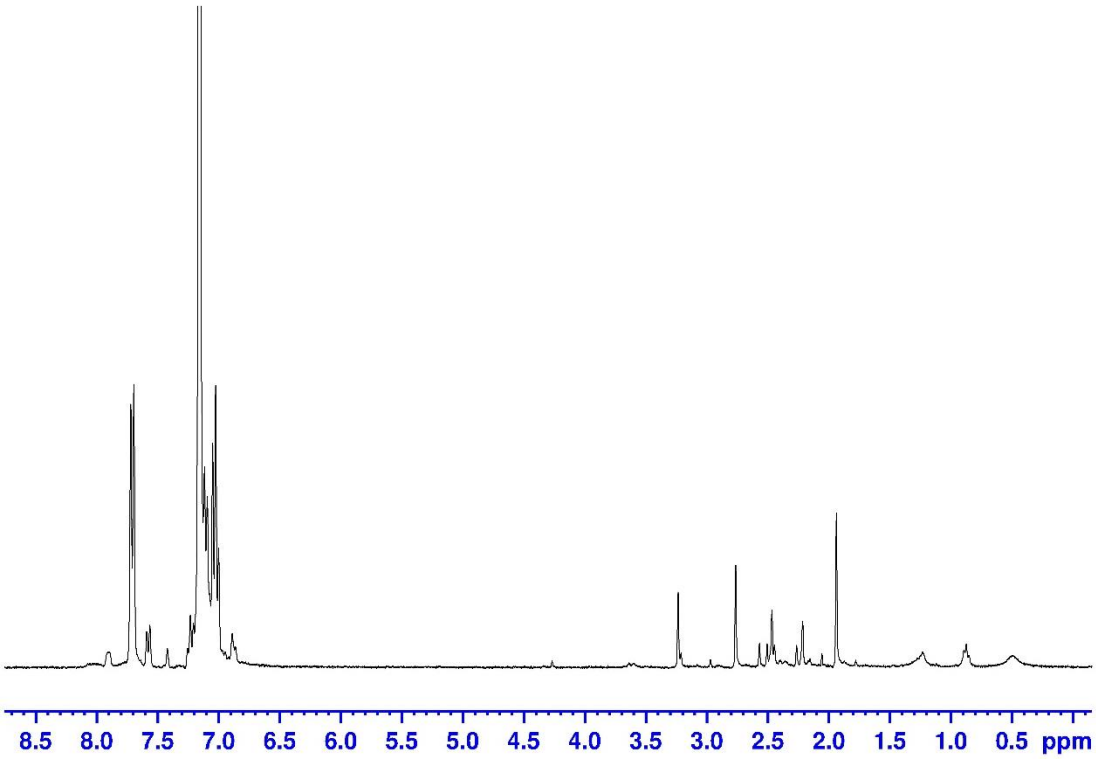


Fig. S12 ^{1}H NMR spectrum of compound **2** after melting in C_6D_6 at room temperature.

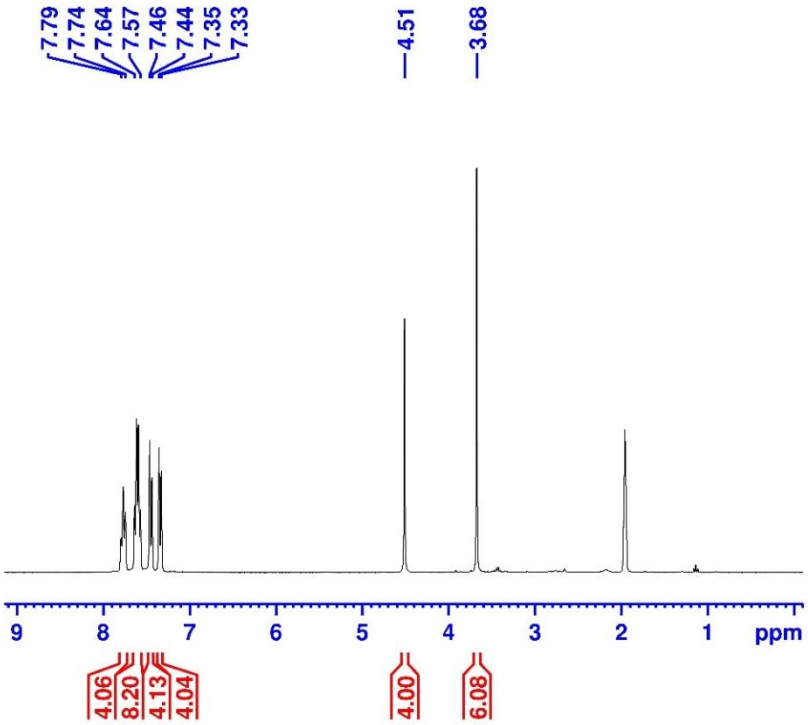


Fig. S13 ^{1}H NMR spectrum of compound **3**$^{(SbF_6)_2}$ in CD_3CN at room temperature.

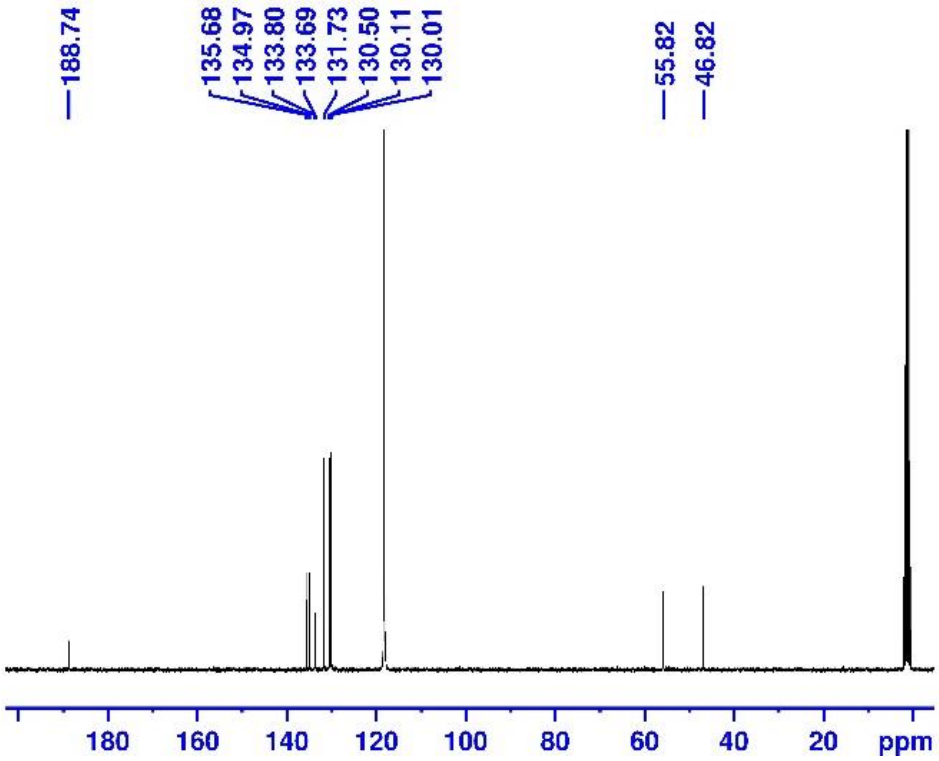


Fig. S14 $^{13}C\{^{1}H\}$ NMR spectrum of compound **3**$^{(SbF_6)_2}$ in CD_3CN at room temperature.

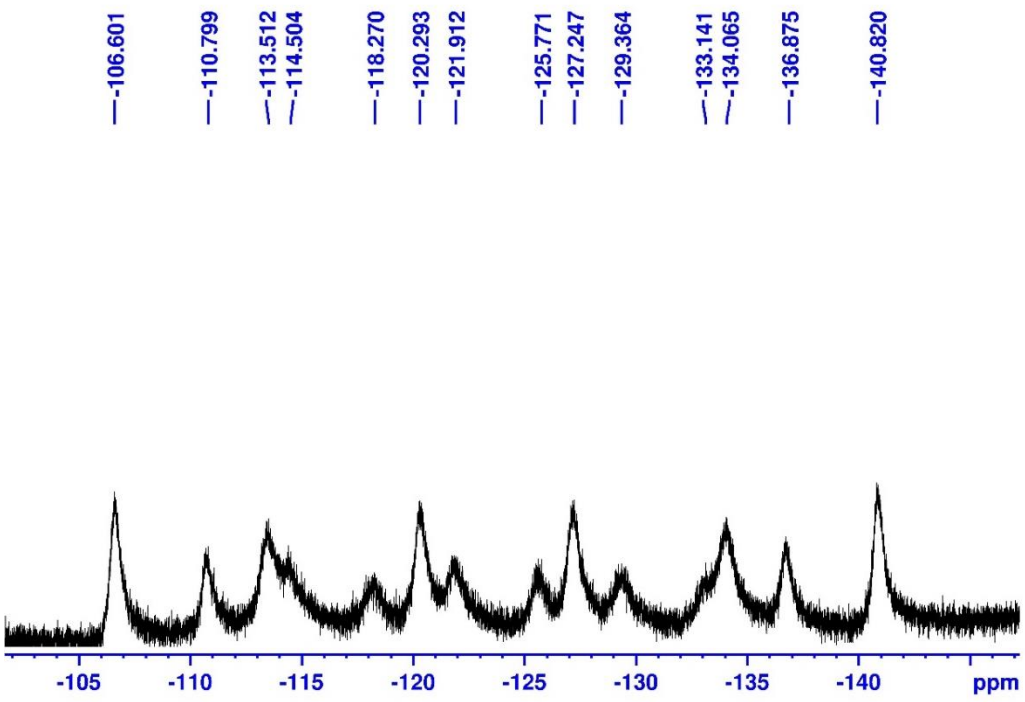


Fig. S15 $^{19}F\{1H\}$ NMR spectrum of compound $\mathbf{3}^{(SbF_6)_2}$ in CD_3CN at room temperature.

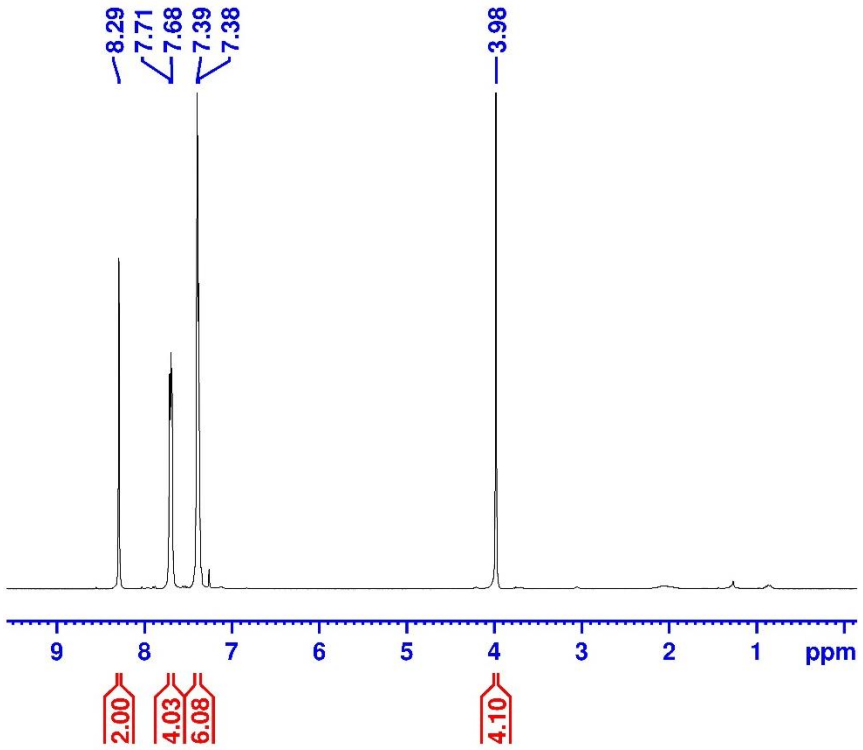


Fig. S16 ^{1}H NMR spectrum of compound *N,N'*-(ethane-1,2-diyl)-bis(1-phenylmethanimine) in $CDCl_3$ at room temperature.

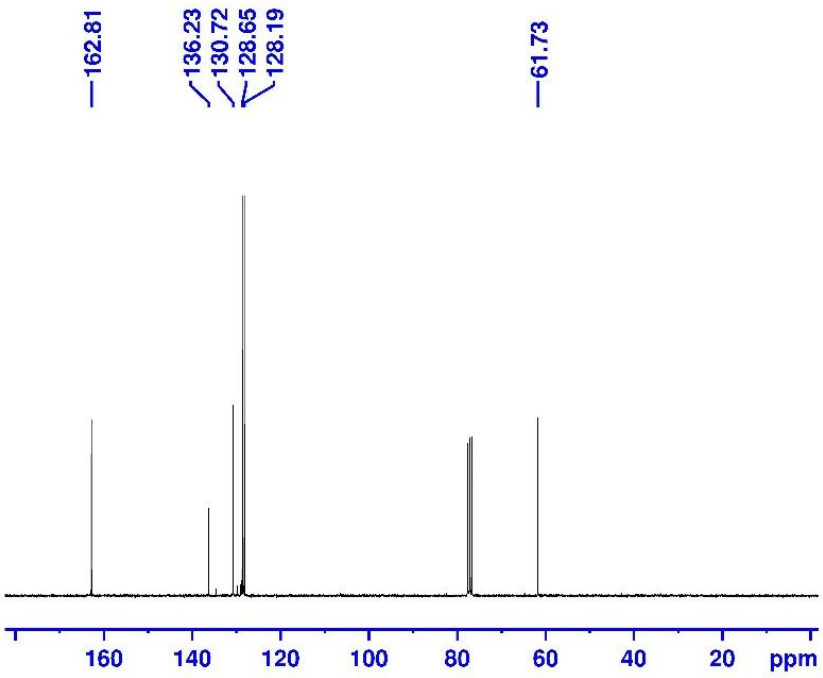


Fig. S17 $^{13}C\{^{1}H\}$ NMR spectrum of compound *N,N'*-(ethane-1,2-diyl)-bis(1-phenylmethanimine) in $CDCl_3$ at room temperature.

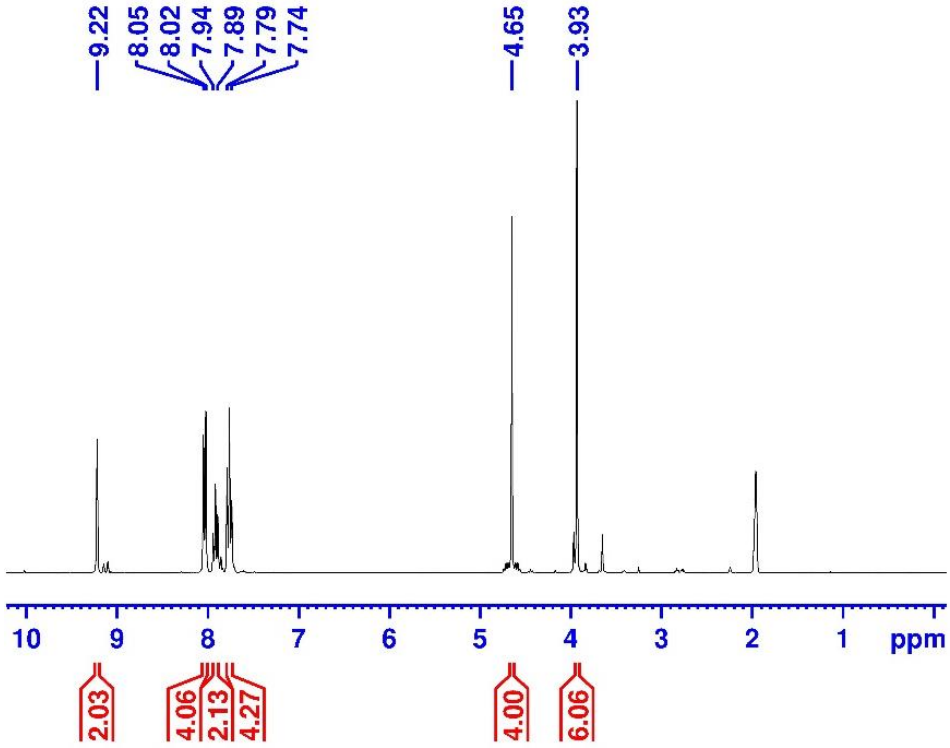


Fig. S18 ^{1}H NMR spectrum of compound **4** in CD_3CN at room temperature.

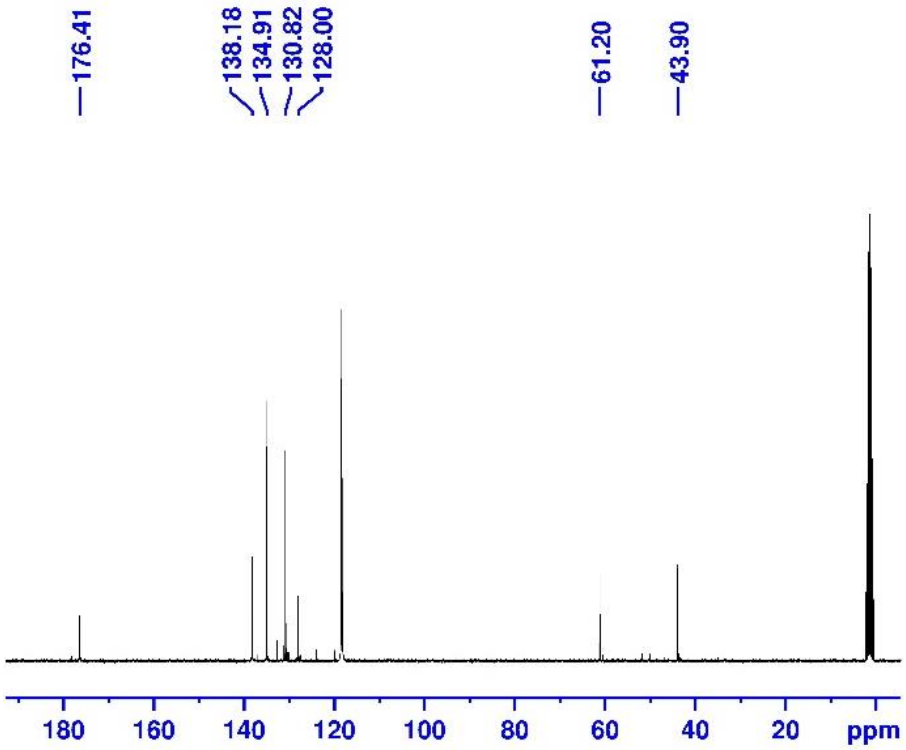


Fig. S19 $^{13}C\{^{1}H\}$ NMR spectrum of compound **4** in CD_3CN at room temperature.

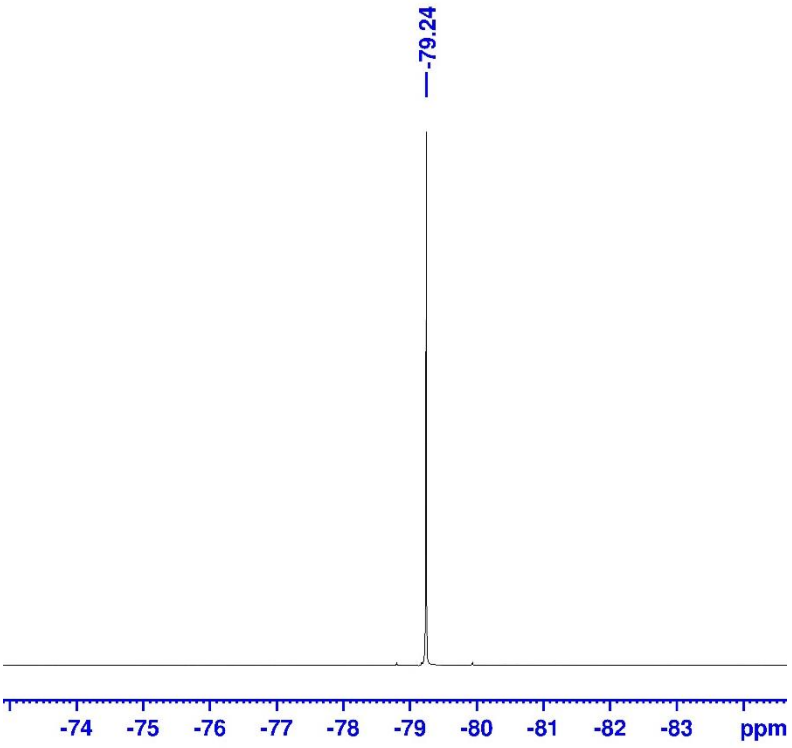


Fig. S20 $^{19}F\{1H\}$ NMR spectrum of compound **4** in CD_3CN at room temperature.

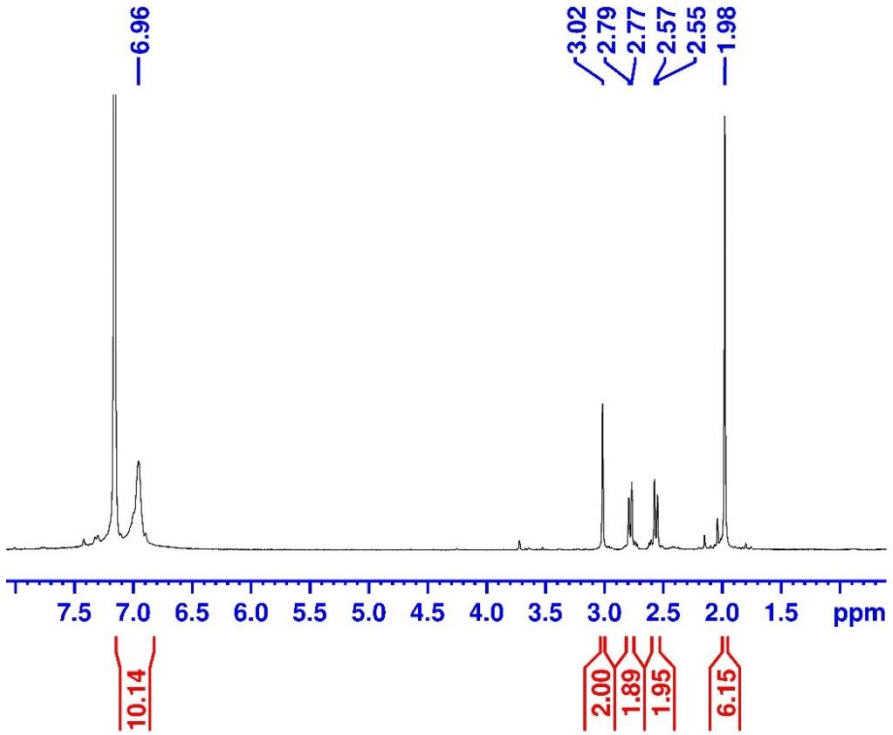


Fig. S21 ^{1}H NMR spectrum of compound **5** in C_6D_6 at room temperature.

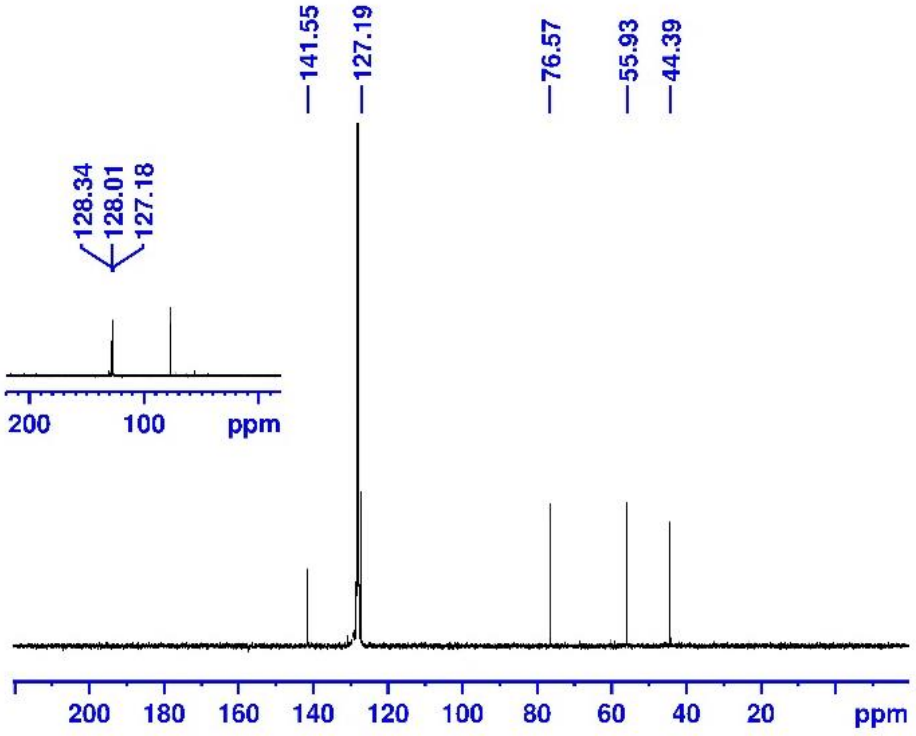


Fig. S22 $^{13}C\{^{1}H\}$ NMR spectrum of compound **5** in C_6D_6 at room temperature (Insert: Dept-90 to showcase the only aromatic C-*H* resonances).

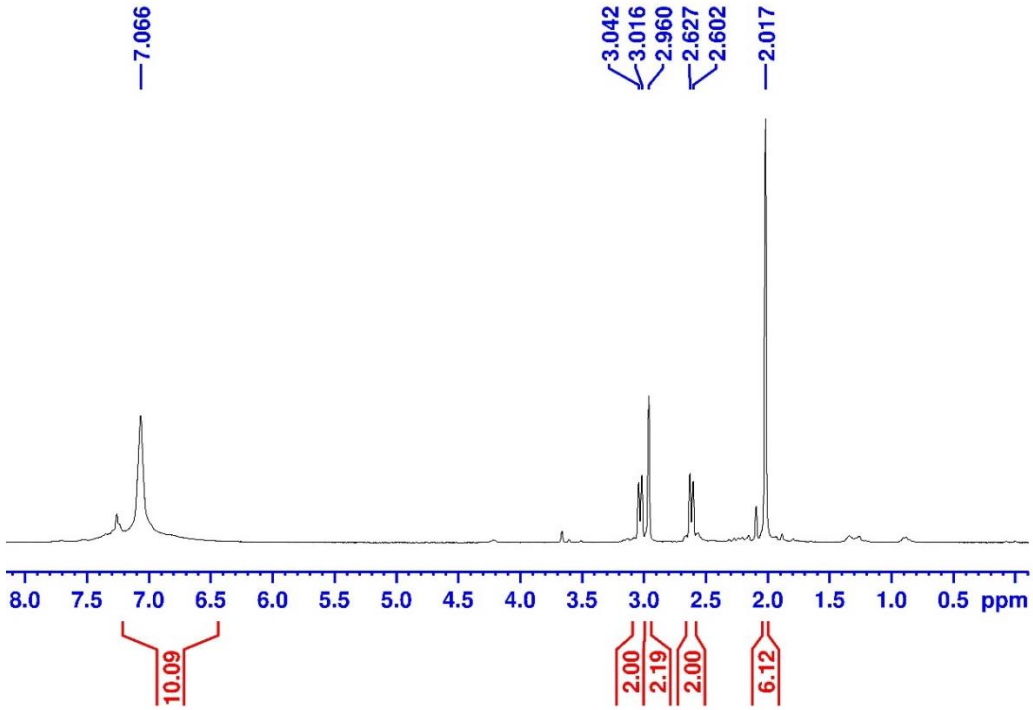


Fig. S23 ^{1}H NMR spectrum of compound **5** in $CDCl_3$ at room temperature.

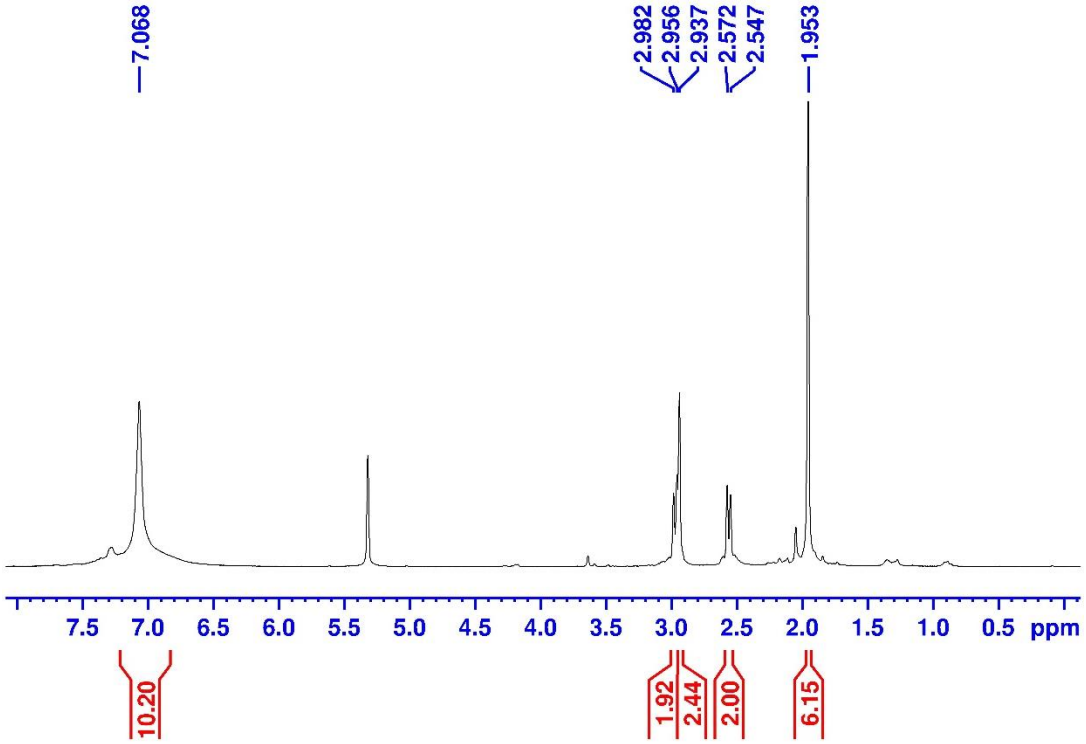


Fig. S24 ^{1}H NMR spectrum of compound **5** in CD_2Cl_2 at room temperature.

FT-IR Spectrum

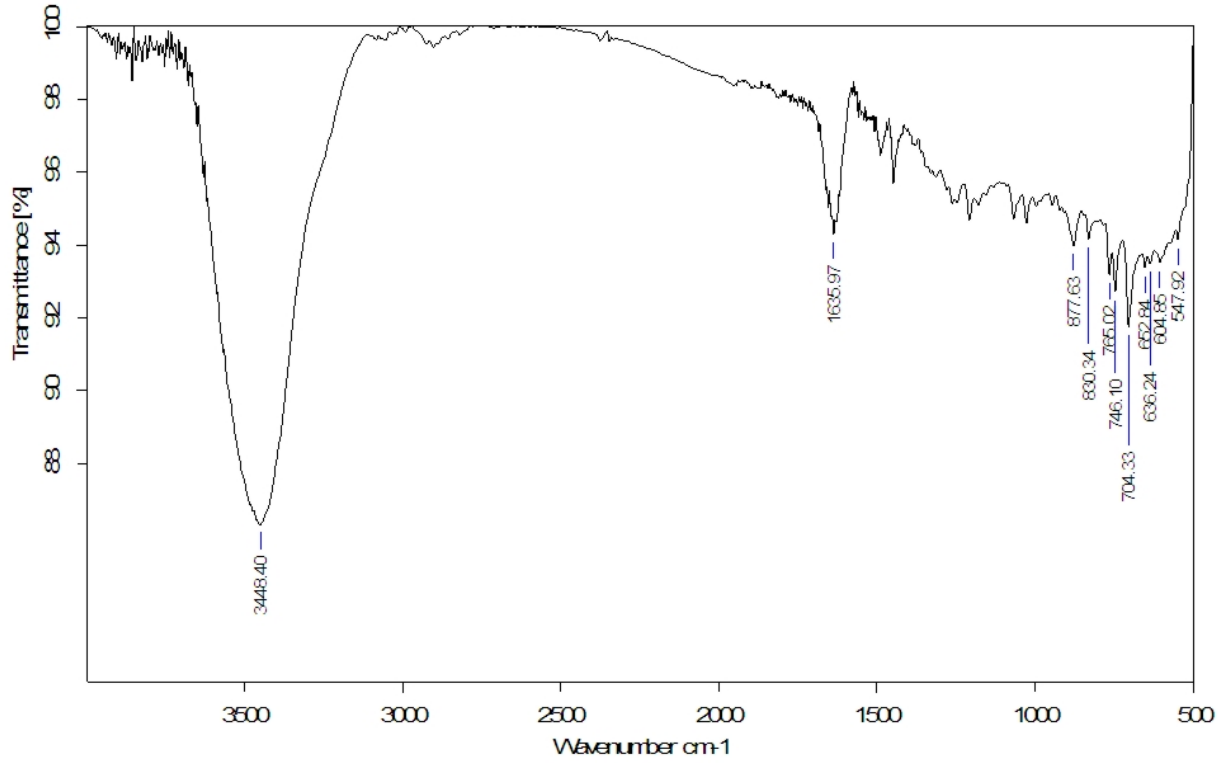


Fig. S25 FT-IR spectrum of compound **2**.

Molecular Structures of 3 $(SbF_6)_2$ and 4

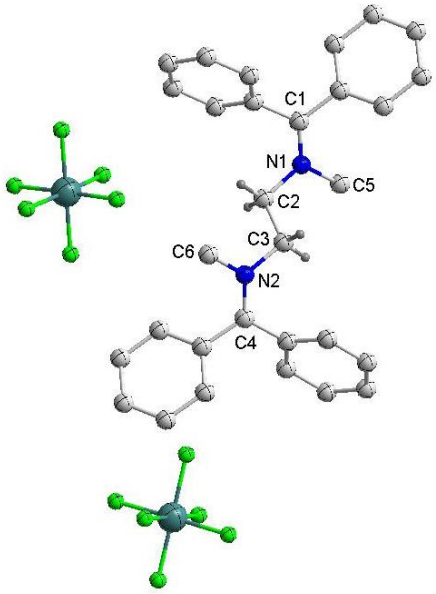


Fig. S26 Molecular structure of **3**$^{(SbF_6)_2}$ with thermal ellipsoids at the 50% probability level. Selected bond lengths (Å) and bond angles (°): C2–C3 1.519(6), N1–C2 1.482(5), N1–C1 1.300(5), N1–C5 1.475(5), C5–N1–C2 114.4(3), C1–N1–C2 122.2(3), N1–C2–C3 110.5(3).

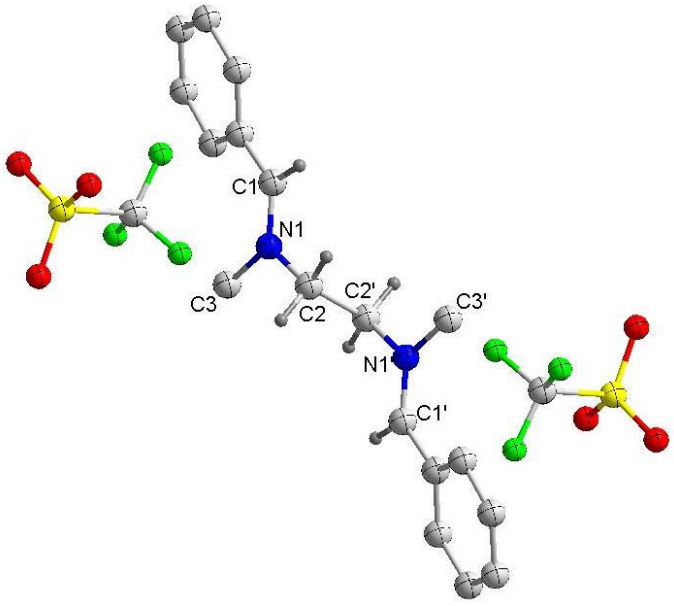


Fig. S27 Molecular structure of **4** with thermal ellipsoids at the 50% probability level. Selected bond lengths (Å) and bond angles (°): C2–C2' 1.530(4), N1–C2 1.474(3), N1–C3 1.474(3), N1–C1 1.297(3), C1–N1–C3 124.6(2), C1–N1–C2 120.0(2), N1–C2–C2'109.6(2), C3–N1–C2 115.5(2).

Crystallographic Details

Single-crystal X-ray diffraction data of **3**, **1**, **2**, **3**$^{(SbF_6)_2}$, **4** and **5** were collected using a Rigaku diffractometer with graphite-monochromated molybdenum *Kα* radiation, λ = 0.71073 Å. Data integration and reduction were processed with CrysAlisPro software.[S2] An empirical absorption correction was applied to the collected reflections with SCALE3 ABSPACK integrated with CrysAlisPro. The structures were solved by direct methods using the SHELXT[S3] program and refined by full matrix least-squares method based on *F*2 by applying the SHELXL[S4] program through the Olex2[S5] interface. All non-hydrogen-atoms were refined with anisotropic displacement parameters. The hydrogen atoms were refined isotropically on calculated positions using a riding model with their *U*iso values constrained to 1.5 *U*eq of their pivot atoms for terminal *sp*3 carbon atoms and 1.2 times for the methylene and the aromatic carbon atoms. Crystal and structure refinement data of all three compounds are summarized in Tables S1-S6.

Compounds **1**, **2**, **3** and **3**$^{(SbF_6)_2}$ (but not **4** and **5**) were all refined with two independent molecules in the unit cell each, which are not identical based on some, and in case of **2** only very subtle, differences in their metrical parameters (i.e. the two molecules in each of the three structures do not match entirely when overlaid). Compound **2** was further refined as merohedral twin with the respective twin law and a minor domain contribution of ca. 10%.

Table S1. Crystal data and structure refinement for compound **3** (CCDC: 2097818).

Identification code	AJ1534	
Empirical formula	$C_{32}H_{30}F_6N_2O_6S_2$	
Formula weight	716.70	
Temperature/K	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
space group	*P -1*	
Unit cell dimensions	a = 9.0759(2) Å.	α = 107.554(2)°.
	b = 12.3329(2) Å	β = 102.974(2)°.
	c = 15.6196(3) Å	γ = 90.901(2)°.
Volume	1617.80(6) $Å^3$	
Z, Calculated density	2, 1.471 g/cm^3	
Absorption coefficient	0.246 mm^{-1}	
F(000)	740	
Crystal size	0.260 x 0.210 x 0.140 mm^3	
Theta range for data collection	2.810 to 28.966°.	
Limiting indices	-11<=h<=12, -16<=k<=16, -21<=l<=19	
Reflections collected / unique	34455 / 7573 [R(int) = 0.0315]	
Completeness to theta= 25.242	99.8%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.68236	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7573 / 0 / 435	
Goodness-of-fit on F^2	1.064	
Final *R* indices [*I*>2sigma(*I*)]	*R1* = 0.0335, *wR2* = 0.0820	
R indices (all data)	*R1* = 0.0396, *wR2* = 0.0850	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.390 and -0.463 e. $Å^{-3}$	

Table S2. Crystal data and structure refinement for compound **1** (CCDC: 2097820).

Identification code	AJ1505	
Empirical formula	$C_{30}H_{30}N_2$	
Formula weight	418.56	
Temperature/K	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
space group	*P -1*	
Unit cell dimensions	a = 8.8709(2) Å	α = 87.090(2)°.
	b = 15.6676(3) Å	β = 88.058(2)°.
	c = 16.3721(4) Å	γ = 86.128(2)°.
Volume	2266.31(9) $Å^3$	
Z, Calculated density	4, 1.227 g/cm^3	
Absorption coefficient	0.071 mm^{-1}	
F(000)	896	
Crystal size	0.260 x 0.210 x 0.150 mm^3	
Theta range for data collection	2.570 to 28.989°.	
Limiting indices	-9<=h<=12, -18<=k<=20, -21<=l<=22	
Reflections collected / unique	33503 / 10375 [R (int) = 0.0286]	
Completeness to theta= 25.242	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.94966	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10375 / 0 / 581	
Goodness-of-fit on F^2	1.079	
Final *R* indices [*I*>2sigma(*I*)]	*R1* = 0.0406, *wR2* = 0.0977	
R indices (all data)	*R1* = 0.0516, *wR2* = 0.1024	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.312 and -0.233 e. $Å^{-3}$	

Table S3. Crystal data and structure refinement for compound **2** (CCDC: 2117405).

Identification code	AJ2019	
Empirical formula	$C_{33}H_{30}N_2O_2$	
Formula weight	450.56	
Temperature/K	250(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
space group	*I a*	
Unit cell dimensions	a = 17.0368(6) Å	α = 90°.
	b = 17.3714(5) Å	β = 104.214(4) °.
	c = 17.3317(7) Å	γ = 90°.
Volume	4972.3(3) $Å^3$	
Z, Calculated density	8, 1.204 g/cm^3	
Absorption coefficient	0.075 mm^{-1}	
F(000)	1920	
Crystal size	0.275 x 0.244 x 0.217 mm^3	
Theta range for data collection	2.703 to 28.929°.	
Limiting indices	-21<=h<=22, -21<=k<=23, -17<=l<=23	
Reflections collected / unique	36487 / 9847 [R(int) = 0.0609]	
Completeness to theta= 25.242	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.58719	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9847 / 2 / 618	
Goodness-of-fit on F^2	1.037	
Final *R* indices [*I*>2sigma(*I*)]	*R1 = 0.0405, wR2 = 0.0979*	
R indices (all data)	*R1 = 0.0567, wR2 = 0.1054*	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.124 and -0.155 e. $Å^{-3}$	

Table S4. Crystal data and structure refinement for compound **3**$^{(SbF_6)_2}$ (CCDC: 2097823).

Identification code	AJ1650	
Empirical formula	$C_{30}H_{30}F_{12}N_2Sb_2$	
Formula weight	890.06	
Temperature/K	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
space group	*P -1*	
Unit cell dimensions	a = 9.3302(2) Å	α = 86.189(2)°.
	b = 15.9677(3) Å	β = 83.167(2)°.
	c = 16.8928(3) Å	γ = 84.182(2)°.
Volume	2482.20(8) Å^3	
Z, Calculated density	3, 1.786 g/cm^3	
Absorption coefficient	1.724 mm^{-1}	
F(000)	1302	
Crystal size	0.240 x 0.210 x 0.170 mm^3	
Theta range for data collection	2.568 to 26.372°.	
Limiting indices	-11<=h<=11, -19<=k<=19, -18<=l<=21	
Reflections collected / unique	40157 / 10104 [R(int) = 0.0900]	
Completeness to theta= 25.242	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.60504	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10104 / 0 / 625	
Goodness-of-fit on F^2	1.069	
Final *R* indices [*I*>2sigma(*I*)]	*R1* = 0.0474, *wR2* = 0.1277	
R indices (all data)	*R1* = 0.0579, *wR2* = 0.1347	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.172 and -1.291 e. Å^{-3}	

Table S5. Crystal data and structure refinement for compound **4** (CCDC: 2097819).

Identification code	AJ1544	
Empirical formula	$C_{20}H_{22}F_6N_2O_6S_2$	
Formula weight	564.51	
Temperature/K	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
space group	*P 21/c*	
Unit cell dimensions	a = 6.4612(17) Å	α = 90°.
	b = 24.723(7) Å	β = 94.82(2)°.
	c = 7.2683(18) Å	γ = 90°.
Volume	1156.9(5) $Å^3$	
Z, Calculated density	2, 1.621 g/cm^3	
Absorption coefficient	0.320 mm^{-1}	
F(000)	580	
Crystal size	0.240 x 0.210 x 0.190 mm^3	
Theta range for data collection	2.931 to 26.368°.	
Limiting indices	-7<=h<=8, -29<=k<=30, -9<=l<=8	
Reflections collected / unique	9389 / 2354 [R(int) = 0.0669]	
Completeness to theta= 25.242	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.51479	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2354 / 0 / 168	
Goodness-of-fit on F^2	1.065	
Final *R* indices [*I*>2sigma(*I*)]	*R1* = 0.0484, *wR2* = 0.1080	
R indices (all data)	*R1* = 0.0603, *wR2* = 0.1122	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.509 and -0.448 e. $Å^{-3}$	

Table S6. Crystal data and structure refinement for compound **5** (CCDC: 2097821).

Identification code	AJ1670R	
Empirical formula	$C_{18}H_{22}N_2$	
Formula weight	266.37	
Temperature/K	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
space group	*P 21/c*	
Unit cell dimensions	a = 16.0877(12) Å	α = 90°.
	b = 5.7417(4) Å	β = 108.833(8)°.
	c = 18.1222(14) Å	γ = 90°.
Volume	1584.3(2) $Å^3$	
Z, Calculated density	4, 1.117 g/cm^3	
Absorption coefficient	0.066 mm^{-1}	
F(000)	576	
Crystal size	0.270 x 0.210 x 0.190 mm^3	
Theta range for data collection	3.080 to 26.369°.	
Limiting indices	-20<=h<=19, -6<=k<=7, -19<=l<=22	
Reflections collected / unique	14432 / 3213 [R(int) = 0.1118]	
Completeness to theta= 25.242	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.26035	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3213 / 0 / 191	
Goodness-of-fit on F^2	1.055	
Final *R* indices [*I*>2sigma(*I*)]	*R1* = 0.0593, *wR2* = 0.1521	
R indices (all data)	*R1* = 0.0708, *wR2* = 0.1623	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.167 and -0.179 e. $Å^{-3}$	

References

S1. I. S. Weitz and M. Rabinovitz, *J. Chem. Soc. Perkin Trans 1,* 1993, 117–120.

S2. CrysAlisPro: Rigaku Oxford Diffraction (1995-2017). Oxford Diffraction Ltd, Abingdon, Oxfordshire, England.

S3. G. M. Sheldrick, *Acta Cryst.* 2015, **A71**, 3–8.

S4. G. M. Sheldrick, *Acta Cryst.* 2015, **C71**, 3–8.

S5. O. V. Dolomanov.; L. J. Bourhis.; R. J. Gildea.; J. A. K. Howard.; H. Puschmann, *J. Appl. Crystallogr.* 2009, **42**, 339–341.